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6B12G2A 6B12G2B
6B12G5 6B12N1 6B1 6B2
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(58) Field of search
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(54) Enzyme detergent composition

(57) A detergent composition comprising an alkali cellulase is particularly effective for removing solid, inorganic dirt and enhances the deterging effect of phosphorus free or low phosphorus content detergents. The cellulase may be obtained from *Bacillus* or *Aeromonas* species.

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The chemical formulae appearing in the printed specification were submitted in formal form after the date of filing.

SPECIFICATION

Detergent composition

The present invention relates to a detergent composition. More particularly, the present invention relates to a detergent composition characterised by conteining en alkali cellulase which exhibits high activity under alkeline conditions.

Recently, techniques of cleansing clothes heve been remerkably developed. The washing of clothes hes been facilitated greatly by the development of detergent materials, weter conditioning, improvements in end increases in the spreed of washing machines and improvements in fibers. Among them, the improvement of the sterting materials for detergents is remarkable. Owing to the improvements in surfectents, builders, dispersants, fluorescent dyes and bleeching agents, the compositions of detergents for clothes heve nearly reached the stege of completion. Detergents for clothes are based on the following principles:

(1) A surfactant or builder is adeorbed on the dirt or/and fiber surface to reduce the surface tension between the dirt or/end fiber and water, so that the dirt is physico-chemically separated out of the fiber.

(2) The dirt is dispersed end solubilized by means of e surfactant or inorganic builder.

(3) The dirt is chemically decomposed by an enzyme such as protease.

(4) Coloured steins are bleached with a bleaching egent.

(5) A fluorescent dye is edsorbed on the fiber surface to brighten it.

(6) The precipitation of active detergent ingredients by divalent metal ions is prevented by means of a cheleting egent.

The fundamentel idee of cleansing clothes in the prior ert is the incorporation of a component which directly attecks the dirt or e component which enhances the attacking power of seid active ingredient in the composition. At present, the effectiveness of the known detergent compositions based on this fundamentel idea heve almost reeched an optimum level and greet efforts will be required if further improvement ere to be mede.

After intensive investigations from viewpoints different from the conventional ideas of the deterging of clothes, the inventors heve found that, unexpectedly, quite excellent deterging effects on types of dirt which are generally not concerned with enzymatic activity of an alkali cellulase (one of the cellulase enzymes) are obtained if the alkali cellulase is incorporeted in a detergent. The present invention has been completed on the basis of this finding.

Commercially eveilable or generelly well-known cellulases heve an optimum pH under acidic or neutrel conditions and their use under alkaline conditions has generally been evoided, since their activity has been reduced under such conditions.

The present invention provides e detergent composition characterised by containing en alkali cellulase heving en alkaline pH as its optimum pH. According to the present invention, there is provided e detergent composition heving e remerkeble deterging effect particularly on inorganic types of dirt which are generally not concerned with alkali cellulase activity et all.

As described above, it hes been known in the ert to use an enzyme es a component of a detergent. As such enzymes, there have been used only those which effectively act on the dirt. More particularly, there have been used only protease for protein stains, emylase for saccharide stains end lipase for olly and fetty steins. Those enzymes ettack the stains directly. Though the mechanism of the deterging effects of the alkali cellulase in the present invention heve not fully been elucidated, it is known that the effects are not merely based on an expansion of the fibers, unlike phenomena observed when surfactants are used.

The main advantages of the present invention are that the detergent is particularly effective for removing solid inorganic dirt such as fine mud particles which cannot be removed sufficiently with conventional detergents and also for removing other types of dirt such as the stains on the necks and cuffs of clothes and olly stains on clothes end that it is highly useful for enhencing the deterging power of phosphorus-free detergents end detergents having only e low phosphorus content. Phosphate salts have been effective for the removel of fine mud particles that has panetrated into the fibers. However, there is nowedays e desire to reduce the amount of phosphete salts incorporated into detergents because of the problem of eutrophication. The requirement for the use of phosphete-free detergents makes the removal of mud particles extremely difficult. In particular, the removel of mud particles from cotton clothing is quite difficult, as is well known. Further, muddy stains on canvas shoes have proved difficult to remove.

The present invention throws a fresh light on the ebove-mentioned problems. According to the present invention, an excellent deterging power equivelent or superior to that of e weak alkaline powdery detergent containing sufficient phosphete salt can be obtained by, for exemple, (1) applying the present invention to an alkeline detergent containing no phosphates or a small amount of phosphates or (2) applying the present invention to a weakly alkaline, liquid, phosphate-free detergent in the cleaning of muddy stains in cellulose fibers or blended fiber cloths comprising cellulose fibers and other fibers.

Another great advantage of the present invention is that it can be epplied to detergents of any

SPECIFICATION
Detergent composition

The present invention relates to a detergent composition. More particularly, the present invention relates to a detergent composition characterised by containing an alkali cellulase which exhibits high activity under alkaline conditions.

Recently, techniques of cleansing clothes have been remarkably developed. The washing of clothes has been facilitated greatly by the development of detergent materials, water conditioning, improvements in and increases in the spread of washing machines and improvements in fibers. Among them, the improvement of the starting materials for detergents is remarkable. Owing to the improvements in surfactants, builders, dispersants; fluorescent dyes and bleaching agents, the compositions of detergents for clothes have nearly reached the stage of completion. Detergents for clothes are based on the following principles:

(1) A surfactant or builder is adsorbed on the dirt or/and fiber surface to reduce the surface tension between the dirt or/and fiber and water, so that the dirt is physico-chemically separated out of the fiber.

(2) The dirt is dispersed and solubilized by means of a surfactant or inorganic builder.

(3) The dirt is chemically decomposed by an enzyme such as protease.

(4) Coloured stains are bleached with a bleaching egent.

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(6) The precipitation of active detergent ingredients by divalent metal ions is prevented by means of a chelating agent.

The fundamental idea of cleansing clothes in the prior art is the incorporation of a component which directly attacks the dirt or a component which enhences the attacking power of said active ingredient in the composition. At present, the effectiveness of the known detergent compositions based on this fundamental idea have almost reached an optimum level and great efforts will be required if further improvement are to be made.

After intensive investigations from viewpoints different from the conventional ideas of the detergng of clothes, the inventors have found that, unexpectedly, quite excellent detergng effects on types of dirt which are generally not concerned with enzymatic activity of an alkali cellulase (one of the cellulase enzymes) are obtained if the alkali cellulase is incorporated in a detergent. The present invention has been completed on the basis of this finding.

Commercially available or generally well-known cellulases have an optimum pH under acidic or neutral conditions and their use under alkaline conditions has generally been avoided, since their activity has been reduced under such conditions.

The present invention provides a detergent composition characterised by containing an alkali cellulase having an alkaline pH as its optimum pH. According to the present invention, there is provided a detergent composition having a remarkable detergng effect particularly on inorganic types of dirt which are generally not concerned with alkali cellulase activity at all.

As described above, it has been known in the art to use an enzyme as a component of a detergent. As such enzymes, there have been used only those which effectively act on the dirt. More particularly, there have been used only protease for protein stains, emylase for saccharide stains and lipase for oily and fatty stains. Those enzymes attack the stains directly. Though the mechanism of the detergng effects of the alkali cellulase in the present invention have not fully been elucidated, it is known that the effects are not merely based on an expension of the fibers, unlike phenomena observed when surfactants are used.

The main advantages of the present invention are that the detergent is particularly effective for removing solid inorganic dirt such as fine mud particles which cannot be removed sufficiently with conventional detergents and also for removing other types of dirt such as the stains on the necks and cuffs of clothes and oily stains on clothes and thet it is highly useful for enhancing the detergng power of phosphorus-free detergents and detergents having only e low phosphorus content. Phosphate salts have been effective for the removal of fine mud particles thet has penetrated into the fibers. However, there is nowadays a desire to reduce the amount of phosphete salts incorporated into detergents because of the problem of eutrophication. The requirement for the use of phosphate-free detergents makes the removal of mud particles extremely difficult. In-particular, the removal of mud particles from cotton clothing is quite difficult, as is well known. Further, muddy stains on canvas shoes have proved difficult to remove.

The present invention throws a fresh light on the ebove-mentioned problems. According to the present invention, an excellent detergng power equivalent or superior to that of e weak alkaline powdery detergent containing sufficient phosphate salt can be obtained by, for example, (1) applying the present invention to an alkaline detergent containing no phosphates or a small amount of phosphates or (2) applying the present invention to a weakly alkaline, liquid, phosphate-free detergent in the cleaning of muddy stains in cellulose fibers or blended fiber cloths comprising cellulose fibers and other fibers.

Another great advantage of the present invention is that it can be applied to detergents of any

[1] Surfactants:

(1) Straight-chain or branched alkylbenzensulfonate salts having an alkyl group of 10—16 carbon atoms in average.

(2) Alkyl or alkenyl ether sulfate salts having a straight-chain or branched alkyl or alkenyl group of 10—20 carbon atoms in average, 0.5—8 mol in average of ethylene oxide, propylene oxide or butylene oxide in the molecule and an addition ratio of ethylene oxide/propylene oxide of 0.1/9.9—9.9/0.1 or ethylene oxide/butylene oxide of 0.1/9.9—9.9/0.1.

(3) Alkyl or alkenyl sulfate salts having an alkyl or alkenyl group of 10—20 carbon atoms in average.

(4) Olefinsulfonate salts having 10—20 carbon atoms in average in the molecule.

(5) Alkanesulfonate salts having 10—20 carbon atoms in average in the molecule.

(6) Saturated or unsaturated fatty acid salts having 10—24 carbon atoms in average in the molecule.

(7) Alkyl or alkenyl ether carboxylate salts having an alkyl or alkenyl group of 10—20 carbon atoms in average, 0.5—8 mol in average of ethylene oxide, propylene oxide or butylene oxide in the molecule and an addition ratio of ethylene oxide/propylene oxide of 0.1/9.9—9.9/0.1 or ethylene oxide/butylene oxide of 0.1/9.9 to 9.9/0.1.

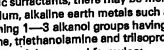
(8) α-Sulfo fatty acid salts or esters of the general formula:

wherein Y represents an alkyl group having 1—3 carbon atoms or a counter-ion, Z represents a counter-ion and R represents an alkyl or alkenyl group having 10—20 carbon atoms.

As the counter-ions of anionic surfactants, there may be mentioned, for example, ions of alkali metals such as sodium and potassium, alkaline earth metals such as calcium and magnesium, ammonium, alkanolamines containing 1—3 alkanol groups having 2 or 3 carbon atoms such as monoethanolamine, diethanolamine, triethanolamine and triisopropanolamine.

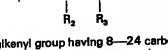
(9) Amino acid-type surfactants of the general formulae:

No. 1



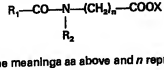
wherein R_1 represents an alkyl or alkenyl group having 8—24 carbon atoms, R_2 represents hydrogen or an alkyl group having 1—2 carbon atoms, R_3 represents an amino acid residue and X represents an alkali metal or alkaline earth metal ion.

No. 2



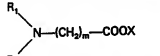
wherein R_1, R_2 and X have the same meaninga as above and n represents an integer of 1—5.

No. 3



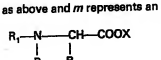
wherein R_1 has the same meaning as above and m represents an integer of 1—8.

No. 4



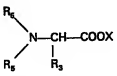
wherein R_1, R_3 and X have the same meaning as above and R_4 represents hydrogen, or an alkyl or hydroxyalkyl group having 1—2 carbon atoms.

No. 5



wherein R_2, R_3 and X have the same meaning as above and R_5 represents a β-hydroxyalkyl or β-hydroxyalkenyl group having 6—28 carbon atoms.

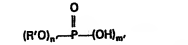
No. 6



wherein R_2, R_5 and X have the same meaning as above.

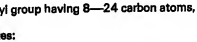
(10) Phosphate ester surfactants:

No. 1 Acid alkyl (or alkenyl) phosphates:



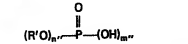
wherein R' represents an alkyl or alkenyl group having 8—24 carbon atoms, n'+m' represents 3 and n' represents a number of 1—2.

No. 2 Alkyl (or alkenyl) phosphates:



wherein R' has the same meaning as above, n"+m" represents a number of 3 and n" represents a number of 1—3.

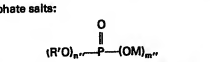
No. 3 Alkyl (or alkenyl) phosphate salts:



wherein R', n" and m" have the same meaning as above and M represents Na, K or Ca.

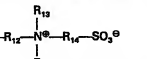
(11) Sulfonic acid-type amphoteric surfactants of the general formulae:

No. 1



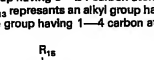
wherein R_{11} represents an alkyl or alkenyl group having 8—24 carbon atoms, R_{12} represents an alkylene group having 1—4 carbon atoms, R_{13} represents an alkyl group having 1—5 carbon atoms, R_{14} represents an alkylene or hydroxyalkylene group having 1—4 carbon atoms.

No. 2



wherein R_{11} and R_{14} have the same meaning as above and R_{15} and R_{16} each represent an alkyl or alkenyl group having 8—24 or 1—5 carbon atoms.

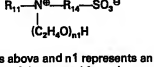
No. 3



wherein R_{11} and R_{14} have the same meaning as above and n1 represents an integer of 1—20.

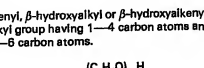
(12) Betaine-type, amphoteric surfactants of the general formulae:

No. 1



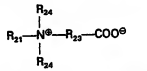
wherein R_{21} represents an alkyl, alkenyl, β-hydroxyalkyl or β-hydroxyalkenyl group having 8—24 carbon atoms, R_{22} represents an alkyl group having 1—4 carbon atoms and R_{23} represents an alkylene or hydroxyalkylene group having 1—6 carbon atoms.

No. 2



wherein R_{21} and R_{23} have the same meaning as above and n2 represents an integer of 1—20.

No. 3



wherein R_{21} and R_{23} have the same meaning as above end R_{24} represents a carboxyalkyl or hydroxyelkyl group having 2—5 carbon atoms.

(13) Polyoxyethylene alkyl or alkenyl ethers having an alkyl or alkenyl group of 10—20 carbon atoms in everege and 1—20 mol of ethylene oxide added.

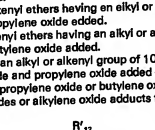
(14) Polyoxyethylene alkylphenyl ethers having an alkyl group of 6—12 carbon atoms in average end 1—20 mol of ethylene oxide edded.

(15) Polyoxypropylene alkyl or alkenyl ethers heving en alkyl or alkenyl group of 10—20 carbon atoms in average and 1—20 mol of propylene oxide added.

(16) Polyoxybutylene alkyl or alkenyl ethers having an alkyl or alkenyl group of 10—20 carbon atoms in average and 1—20 mol of butylene oxide added.

(17) Nonionic surfactants having an alkyl or alkenyl group of 10—20 carbon atoms in averege and 1—30 mol in total of ethylene oxide and propylene oxide added or ethylene oxide and butylene oxide edded (ratio of ethylene oxide to propylene oxide or butylene oxide being 0.1/9.9 to 9.9/0.1).

(18) Higher fatty acid alkanolamides or alkylene oxide adducts thereof of the general formula:



wherein R'_{11} represents an alkyl or alkenyl group having 10—20 carbon atoms, R'_{12} represents H or CH_3, n3 represents an integer of 1—3 and m3 represents an integer of 0—3.

(19) Sucrose/fatty acid esters comprising fatty acids having 10—20 carbon atoms in average and sucrose.

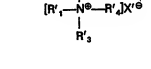
(20) Fatty acid/glycerol monoesters comprising fatty acids having 10—20 carbon atoms in average and glycerol.

(21) Alkylemine oxides of the general formula:

wherein R'_{13} represents an alkyl or alkenyl group having 10—20 carbon atoms and R'_{14} and R'_{15} each represent an alkyl group having 1—3 carbon atoms.

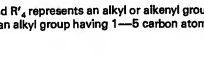
(22) Cetionic surfactants of the general formulae:

No. 1



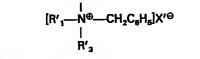
wherein at least one of R'_1, R'_2, R'_3 and R'_4 represents an alkyl or alkenyl group having 8—24 carbon atoms and the remainder represents an alkyl group having 1—5 carbon atoms and X' represents a halogen.

No. 2



wherein R'_1, R'_2, R'_3 and X' have the same meaning as above.

No. 3



wherein R'_1, R'_2 and X' have the same meaning as above, R'_5 represents an alkylene group having 2—3 carbon atoms and n4 represents an integer of 1—20.

The composition preferably contains at least one of the above surfactants in an amount of at least 10 wt.%.

As preferred surfactants, there may be mentioned above surfactants 1), 2), 3), 4), 5), 6), 11)-No. 2, 12)-No. 1, 13), 14), 15), 17) and 18).

[2] Divalent metal ion sequestering agents:

The composition may contain 0—50 wt.% of one or more builder components selected from the group consisting of alkali metal salts or alkanolamine salts of the following compounds:

1) Salts of phosphoric acids such as orthophosphoric acid, pyrophosphoric acid, tripolyphosphoric acid, metephosphoric acid, hexametaphosphoric acid and phytic acid.

2) Salts of phosphonic acids such as ethane-1,1-disphosphonic acid, ethane,1,1,2-triphosphonic acid, ethane-1-hydroxy-1,1-diphosphonic acid and its derivatives, ethane-hydroxy-1,1,2-triphosphonic acid, ethane-1,2-dicarboxy-1,2-diphosphonic acid and methanehydroxyphosphonic acid.

3) Salts of phosphono carboxylic acids such as 2-phosphonobutane-1,2-dicarboxylic acids, 1-phosphonobutane-2,3,4-tricarboxylic acids and α-methylphosphonosuccinic acid.

4) Salts of amino acids such as aspartic acid, glutamic acid and glycine.

5) Salts of aminopolyacetic acids such as nitrilotriacetic acid, iminodiacetic acid, ethylenediaminetetraacetic acid, diethylenetriaminepentaacetic acid, glycol ether diaminetetraacetic acid, hydroxyethyliminodiacetic acid, triethylenetetraminehexaacetic acid and dienkolic acid.

6) High-molecular electrolytes such as polyacrylic acid, polyaconitic acid, polyitaconic acid, polycitractonic acid, polyfumaric acid, polymeleic acid, polymesaconic acid, poly-α-hydroxyacrylic acid, polyvinylphosphonic acid sulphonated polymaleic acid, maleic anhydride/diisobutylene copolymer, maleic anhydride/styrene copolymer, maleic anhydride/methyl vinyl ether copolymer, maleic anhydride/ethylene copolymer, maleic anhydride/ethylene cross-linked copolymer, maleic anhydride/vinyl acetate copolymer, maleic anhydride/acrylonitrile copolymer, maleic anhydride/acrylate ester copolymer, maleic anhydride/butadiene copolymer, maleic anhydride/isoprene copolymer, poly-β-keto carboxylic acid derived from maleic anhydride and carbon monoxide, itaconic acid/ethylene copolymer, itaconic acid/aconitic acid copolymer, itaconic acid/maleic acid copolymer, itaconic acid/acrylic acid copolymer, malonic acid/methylene copolymer, meseconic acid/fumaric acid copolymer, ethylene glycol/ethylene terephthelate copolymer, vinylpyrrolidone/vinyl acetate copolymer, 1-butene-2,3,4-tricarboxylic acid/itaconic acid/acrylic acid copolymer, quaternary ammonium group-containing polyester polyaldehyde carboxylic acids, cis-isomer of epoxysuccinic acid, poly[N,N-bis(carboxymethyl)acrylamide], poly(hydroxy carboxylic acid), starch succinate, starch maleate, starch terephthalate, starch phosphate ester, dicarboxystarch, dicarboxymethylstarch and cellulose succinate esters.

7) Non-dissociating high-molecular compounds such as polyethylene glycol, polyvinyl alcohol, polyvinylpyrrolidone and cold water-soluble, urethenated polyvinyl alcohol.

8) Salts of dicarboxylic acids such as oxalic acid, melonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid and decane-1,10-dicarboxylic acid; salts of diglycolic acid, thiodiglycolic acid, oxalacetic acid, hydroxydisuccinic acid, carboxymethylhydroxysuccinic acid and carboxymethyltertronic acid; salts of hydroxy carboxylic acids such as glycolic acid, malic acid, hydroxpivalic acid, tartaric acid, citric acid, lactic acid, gluconic acid, mucic acid, glucuronic acid and dialdehyde starch oxide; salts of itaconic acid, methylsuccinic acid 3-methylglutaric acid, 2,2-dimethylmalonic acid, maleic acid, fumaric acid, glutamic acid, 1,2,3-propanetricarboxylic acid, aconitic acid, 3-butena-1,2,3-tricarboxylic acid, butane,1,2,3,4-tetracarboxylic acid,

ethanetetracarboxylic acid, ethanetetracarboxylic acid, n-alkenylaconitic acid, 1,2,3,4-cyclopentanetetracarboxylic acid, phthalic acid, trimesic acid, hemimellitic acid, pyromellitic acid, benzenehexacarboxylic acid, tetrahydrofuran-1,2,3,4-tetracarboxylic acid and tetrahydrofuran-2,2,5,5-tetracarboxylic acid; salts of sulfonated carboxylic acids such as sulfotaconic acid, sulfotricarballylic acid, cysteic acid, sulfoacetic acid and sulfosuccinic acid; carboxymethylated sucrose, lactose and raffinose, carboxymethylated pentaerythritol, carboxymethylated gluconic acid, condensates of polyhydric alcohols or saccharids with maleic anhydride or succinic anhydride, condensates of hydroxy carboxylic acids with maleic anhydride or succinic anhydride, and organic acid salts such as CMOS and Builder M.

9) Aluminosilicates:

No. 1 Crystalline aluminosilicates of the formula:

$$x'(m'_2O \text{ or } M''O) \cdot Al_2O_3 \cdot y'(SiO_2) \cdot w'(H_2O)$$

wherein M' rapresents an alkali metal atom, M" represents an alkaline earth metal atom exchangeable with calcium, and x', y' and w' represent mole numbers of the respective components and generally, they are as follows: $0.7 \leqq x' \leqq 1.5$, $0.8 \leqq y' \leqq 6$ and w' being a positive number.

No. 2 Detergent builders having the following general formula are particularly preferred:

$$Na_2O \cdot Al_2O_3 \cdot nSiO_2 \cdot wH_2O$$

wherein n represents a number of 1.8—3.0 and w represents a number of 1—6.

No. 3 Amorphous aluminosilicates of the formula:

$$x(M_2O) \cdot Al_2O_3 \cdot y(SiO_2) \cdot w(H_2O)$$

wherein M represents sodium and/or potassium atom, and x, y and w represent mole numbers of the respective components within the following ranges:

$$0.7 \leqq x \leqq 1.2$$

$$1.6 \leqq y \leqq 2.8$$

w: any positive number including 0.

No. 4 Amorphous aluminosilicates of the formula:

$$X(M_2O) \cdot Al_2O_3 \cdot Y(SiO_2) \cdot Z(P_2O_5) \cdot \omega(H_2O)$$

wherein M represents Na or K and X, Y, Z and ω represent mole numbers of the respective components within the following ranges:

$$0.20 \leqq X \leqq 1.10$$

$$0.20 \leqq Y \leqq 4.00$$

$$0.001 \leqq Z \leqq 0.80$$

ω: any positive number including 0.

[3] Alkalis or inorganic electrolytes:

The composition may contain also 1—50 wt.%, preferably 5—30 wt.%, of one or more alkali metal salts selected from the following compounds as the alkali or inorganic electrolyte: silicates, carbonates and sulfates. Further, the composition may contain organic alkalis such as triethanolamine, diethanolamine, monoethanolamine and triisopropanolamine.

[4] Antiredeposition agents:

The composition may contain 0.1—5% of one or more of the following compounds as antiredeposition agent(s): polyethylene glycol, polyvinyl alcohol, polyvinylpyrrolidone and carboxymethylcellulose.

Particularly, a combination of carboxymethylcellulose or polyethylene glycol with the alkali cellulose of the present invention exhibits a synergism in the removal of muddy dirts.

In order to avoid the decomposition of carboxymethylcellulose by the alkali cellulose in the detergent composition, it is preferred that the carboxymethylcellulose is used in a granular or coated form.

[5] Bleaching agents:

A combination of the alkali cellulase of the present invention with a bleaching agent such as sodium percarbonate, sodium perborate, sodium sulfate/hydrogen peroxide adduct or sodium chloride/hydrogen peroxide adduct or/and a photosensitive bleaching dye such as zinc or aluminum salt of sulfonated phthalocyanine further improves the deterging effects.

[6] Enzymes (enzymes which exhibits the essential enzymatic effects thereof in the deterging step):

As the enzymes, the following enzymes may be mentioned (classified with respect to their enzymatic reactivities):

Hydrolases, hydrases, oxido-reductases, desmolases, transferases and isomerases. All of these enzymes may be used in the present invention. Particularly preferred enzymes are hydrolases such as proteases, esterases, carbohydrolases and nucleases.

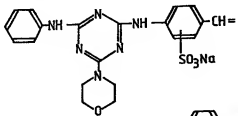
Examples of proteases are pepsin, trypsin, chymotrypsin, collagenase, keratinase, elastase, subtilisin, BPN, papain, bromalin, carboxypeptidases A and B, aminopeptidase and aspergillopeptidase A and B.

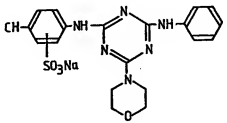
Examples of esterases are gastric lipase, pancreatic lipase, vegetable lipases, phospholipases, cholinesterases and phosphotases.

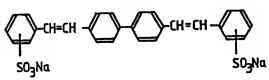
Carbohydrolases other than alkali cellulases include maltase, saccharase, amylase, pectinase, lysozyme, α-glucosidase and β-glucosidase.

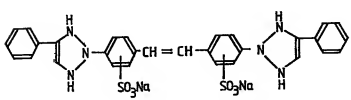
[7] Bluing agents and fluorescent dyes:

Various bluing agents and fluorescent dyes may be incorporated in the composition, if necessary. For example, compounds of the following structures are recommended:

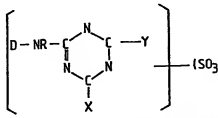




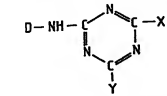




and bluing agents of the general formulae:



wherein D represents a residue of blue or purple, monoazo, disazo or anthraquinone dye, X and Y each represent hydroxyl group, amino group, an aliphatic amino group which may be substituted with hydroxyl, sulfonic acid, carboxylic acid or alkoxyl group, or an aromatic or alicyclic amino group which may be substituted with a halogen atom or hydroxyl, sulfonic acid, carboxylic acid, lower alkyl or lower alkoxyl group, R represents a hydrogen atom or a lower alkyl group but excluding cases wherein (1) R represents a hydrogen atom and both X and Y represent a hydroxyl group or an alkanolamine at the same time and (2) R represents a hydrogen atom, one of X and Y represents a hydoxyl group and the other represents an alkanolamine group, and *n* represents an integer of at least 2, and



wherein D represents a residue of a blue or purple, azo or anthraquinone dye, and X and Y may be the same or different and represent an alkanolamine residue or a hydroxyl group.

[8] Caking-preventing agents:

The following caking-preventing agents may be incorporated in powdery detergent composition: p-toluenesulfonate salts, xylenesulfonate salts, acetate salts, sulfosuccinate salts, talc, finly pulverized silica, clay, calcium silicates (such as Micro-cell of Johns-Manvill Co.), calcium carbonate and magnesium oxide.

[9] Masking agents for factors inhibiting the alkali cellulase activity:

The alkali cellulases are deactivated in some cases in the presence of copper, zinc, chromium, mercury, lead, manganese or silver ions or their compounds. Various metal chelating agents and metal-precipiteting agents are effective on these inhibitors. They include, for example, divalent metal ion sequestering agents as listed in the above item [2] with reference to optional additives as well as magnesium silicate and magnesium sulfate.

Cellobiose, glucose and gluconolactone act sometimes as the inhibitors. It is preferred to avoid the co-presence of those saccharides with the alkali cellulase as far as possible. In case the co-presence is unavoidable, it is necessary to avoid the direct contact of the saccharides with the alkali cellulase by, for example, coating them.

Strong chelating agents such as ethylenediaminetetraacetate salts, anionic surfactants and cationic surfactants act as the inhibitors in some cases. However, the co-presence of those substances with the alkali cellulase is allowable if the direct contact of them is prevented by some ideas such as tableting and coating methods.

The above-mentioned masking agents and methods may be employed, if necessary, in the present invention.

[10] Alkali cellulase-activators:

The activators vary depending on variety of the alkali cellulases. In the presence of proteins, cobalt and its salts, calcium and its salts, potassium and its salts, sodium and its salts or monosaccharides such as mannose and xylose, the alkali cellulases are activated and their detergng powers are improved remarkably.

[11] Antioxidants:

The antioxidants include, for example, tert-butylhydroxytoluene, 4,4'-butylidenebis(6-tert-butyl-3-methylphenol), 2,2'-butylidenebis(6-tert-butyl-4-methylphenol), monostyrenated cresol, distyrenated cresol, monostyrenated phanol, distyrenated phenol and 1,1'-bis(4-hydroxyphenyl)cyclohexane.

[12] Solubilizers:

The solubilizers include, for example, lower alcohols such as ethanol, benzenesulfonate salts, lower alkylbenzenesulfonate salts such as p-toluenesulfonate salts, glycols such as propylene glycol, ecetylbenzenesulfonate salts, acetamides, pyridinedicarboxylic acid amides, benzoate salts and urea.

The following examples will further illustrate the present invention. In the following referentiel example, the preparation of an alkali cellulase le explained. Unless otherwise state, percentages in the following examples are given by weight.

Referential Example 1

Preparation of alkali cellulase:

Alkali-resistant cellulases according to the present invention are obtained by, for example, a technique disclosed in G. Okada, T. Nishizewa and K. Nishizawa "Biochem. J., *99*, 214 (1966)". More particularly, a crude enzyme solution was extracted from the hepatopancreas of a marina mollusc (Dolabella sp.). The crude enzyme solution was subjected to the starch zona-electrophoresis and carboxymethylcellulose-saccharifying activity of the resulting fraction was measured. The carboxymethylcellulose-saccharifying activity of pH 8.3 was determined from an absorbance (ΔOD) at 660 mμ using an alkaline copper reagent and arsenomolybdate after reacting the fraction with carboxymethylcellulose.

Fraction No.	*Cellulase Activity at pH 8.3 (ΔOD)*
10	0.05
15	0.55
20	0.47
30	0.40
35	0.12

It is understood that fractions Nos. 15, 20 and 30 contain cellulases having a high activity under a weak alkaline condition.

Example 1

Effects of alkali cellulase superior to those of other enzymes on cotton cloths artificially stained with muddy dirts will be shown:

1) Detergent compositions:

	A (%)	*B (%)*
Sodium straight-chain dodecylbenzenesulfonate	10	—
Sodium α-olefinsulfonates (C_{16-18})	5	—
Sodium alkylethoxysulfates (C_{14-15}, $\overline{EO}$=1.5 mole)	2	25
Sodium alkyl sulfates (C_{14-15})	3	—
Soap (beef fatty acid sodium salts)	2	—
Secondary alcohol (C=13.5) ethoxylate ($\overline{EO}$=7)	—	25
Sodium tripolyphosphate	10	—
Crystalline sodium aluminosilicate (type 4A)	10	—
Sodium silicate	10	—
Triethanolamine	—	5
Sodium carbonate	10	—
Potassium carbonate	—	5
Carboxymethylcellulose	1	1
Polyethylene glycol ($\overline{MW}$ 6000)	1	1
Fluorescent dye	0.4	0.3
Bluing agent	—	0.05
Sodium p-toluenesulfonate	2	—
Ethanol	—	8
Water	10	balance
Enzyme	0 or 3	0 or 2
Perfume	0.2	0.1
Glauber's salt	balance	—

2) Mud-stained cloths (artificially stained cloths):

Kanuma sekiguyoku soil for horticultural use was dried at 120°C±5°C for 4 h and then pulverized. 150 mesh (100 μm)-passed soil particles were dried at 120°C±5°C for 2 h. 150 g of the soil particles was dispersed in 1000 l of Perclene. A calico #2023 cloth was contacted with the dispersion and brushed. After removal of the dispersion, excessive mud remaining on the cloth was removed (Japanese Patent Laid-Open No. 26473/1980).

Test pieces having a size of 10 cm×10 cm were prepared and subjected to the tests.

3) Deterging conditions and method and appraisal:

A detergent was dissolved in 4°DH hard water to obtain 1 l of 0.133% aqueous detergent solution. Five pieces of the cloth artificially stained with the muddy dirt were immersed in the aqueous detergent solution. After leaving them to stand at 40°C for 2 hours, the detergent solution and the pieces of artificially stained cloth were transferred in a stainless steel beaker for Turgotometer and stirred at 100 rpm at 20°C for 10 minutes in the Turgotometer. After washing with running water, they were pressed with an iron and their reflectivities were measured. The deterging rate was calculated according to the following formula:

Reflectivities of the original cloth before the washing and those of the stained cloth before and after the washing were measured by means of an automatic recording colorimeter (a product of Shimadzu Seisaku-sho) and the deterging rate (%) was calculated according to the following formula:

$$\text{Deterging rate (\%)} = \frac{\text{(Reflectivity after washing)} - \text{(Reflectivity before washing)}}{\text{(Reflectivity of original cloth)} - \text{(Reflectivity before washing)}} \times 100$$

An average of fives samples was shown in Table 1.

The aqueous detergent solution before the washing had pH 10.6.

4) Enzymes used:

(1) Not used (balanced with Glauber's salt) (comparative)
(2) Alkali cellulase (crude enzyme solution of fraction No. 15 in the above referential example) } Present invention
(3) Alkali cellulase (crude enzyme solution of fraction No. 20 in the above referential example) } Present invention
(4) Alkali cellulase (crude enzyme solution of fraction No. 30 in the above referential example) } Present invention
(5) Cellulase (crude enzyme solution of fraction No. 35 in the above referential example)
(6) Amylase (Termamyl 60 G; a product of Novo Co.)
(7) Protease (Gist Brocades, maxatase P 330,000)
(8) Lipase (Ollpase; a product of Nagase Sangyo Co.)

5) Results:

Table 1

Enzyme in the Detergent	Deterging rate (%) Composition A	Composition B
①	65	60
②	81	78
③	80	77
④	79	76
⑤	74	72
⑥	66	—
⑦	65	—
⑧	65	—

Referential Example 2

A culture medium (having a pH value of 10) containing 1.0% of peptone, 1.0% of meat extract, 1.0% of carboxymethyl cellulose (CMC), 0.5% of sodium chloride, 0.1% of potassium dihydrogen phosphate and 1.0% of anhydrous sodium carbonate was inoculated with *Bacillus* N4, a novel species belonging to the genus *Bacillus* (deposited with the FRI deposition number of 1141), separated from the soil collected at Hirosawa, Wako city, Saitama prefecture, and shaking culturing was carried out 37°C for 72 hours. Cells were removed by centrifugal separation to obtain a crude enzyme. The crude enzyme was dried with ethanol according to the customary method to obtain a cellulase powder. Thus, 10 g/l of a cellulase enzyme (having an enzymatic activity of 0.6 unit/mg of the solid at a pH value of 6) (hereinafter referred to as "cellulase N-4") was obtained.

At a pH value of 9, the so-obtained enzyme retained 85% of the activity at a pH value of 6.

Incidentally, a commercially available cellulase originating from *Aspergillus niger* had an activity of 0% at a pH value of 9. That is, the cellulase had no activity at a pH value of 9.

Referential Example 3

A flask was charged with 9 ml of a culture medium containing 0.5% of ammonium sulfate, 1.5% of pulp block, 0.02% of glucose, 0.1% of yeast extract, 0.02% of $MgSO_4 \cdot 7H_2O$ and 0.2% of K_2HPO_4 and the culture medium was sterilized at 120°C for 20 minutes. The sterilized culture medium was cooled and mixed with 10 ml of 0.7% aqueous solution of $NaHCO_3$ separately sterilized. The culture medium was then inoculated with a cellulase 212-producing species belonging to the genus *Aeromonas* (deposited with the FRI deposition number of 2306), and shaking culturing was carried out at 37°C for 72 hours. Cells were removed by centrifugal separation to obtain a crude enzyme liquid of cellulase 212. The crude enzyme liquid was dried with ethanol according to the customary procedure to obtain a cellulase powder having an enzymatic activity of 0.55 unit/mg of the solid at a pH value of 6 (hereinafter referred to as "cellulase 212"). At a pH value of 9, the so-obtained enzyme retained 70% of the enzymatic activity at a pH value of 6.

Enzymes used in Examples 2 to 7 are listed as follows.

(1) Cellulase N4
(2) Cellulase 212
(3) Cellulase (supplied by Sigma Co., originating from *Aspergillus niger*, 1.35 units/mg)
(4) Lipase (supplied by Gist Brochades NV, originating from *R. oryzae*)
(5) Amylase (Termamil 60G supplied by Novo Industries Co.)
(6) Protease (Alkalase 2.0M supplied by Novo Industries Co.)

Example 2

A highly alkaline powdery detergent for clothing was prepared according to the following recipe. The pH value of a 0.133% aqueous solution of the detergent was 11.2.

Sodium linear-dodecylbenzene-sulfonate	20% by weight
Soap (sodium salt of beef tallow fatty acid)	2% by weight
Sodium orthophosphate	20% by weight
Sodium metaphosphate	10% by weight
Sodium carbonate	15% by weight
Carboxymethyl cellulose	1% by weight
Polyethylene glycol	1% by weight
Fluorescent dye	0.4% by weight
Glauber salt	balance
Enzyme	0 or 2% by weight
Water	5% by weight

The results of the washing test made on so-prepared detergents are shown in Table 2.

Incidentally, in Table 2 and Tables given hereinafter, each detergent is identified by example number-enzyme number (the enzyme-free detergent is identified by example number—(0)).

Table 2

Detergent	*Washing Power Index*
1—(0) (reference detergent)	100
1—(1) (present invention)	103.5
1—(2) (present invention)	104.0
1—(3)	101
1—(4)	100
1—(5)	100
1—(6)	100.5

Example 3

A weakly alkaline powdery detergent for clothing was prepared according to the following recipe. The pH value of a 0.133% aqueous solution of the detergent was 10.3.

Sodium α-olefin-sulfonate	20% by weight
Soap	1% by weight
Sodium tripolyphosphate	20% by weight
Sodium silicate (JIS No. 2)	10% by weight
Sodium carbonate	5% by weight
Carboxymethyl cellulose	1% by weight
Polyethylene glycol	1% by weight
Fluorescent dye	0.4% by weight
Glauber salt	balance
Enzyme	0 or 2% by weight
Water	10% by weight

In the same manner as described in Example 1, the washing test was carried out. The obtained results are shown in Table 3.

Table 3

Detergent	*Washing Power Index*
2—(0) (reference detergent)	100
2—(1) (present invention)	104
2—(2) (present invention)	104.5
2—(4)	100
2—(5)	100
2—(6)	100.5

Example 4

A neutral powdery detergent for clothing was prepared according to the following recipe. The pH value of a 0.133% aqueous solution of the detergent was 6.8

Sodium linear-alcohol (C=14) sulfate	30% by weight
Polyethylene glycol	1% by weight
Sodium phosphate	1% by weight
Fluorescent dye	0.2% by weight
Glauber salt	balance
Enzyme	0 or 2% by weight
Water	5% by weight

The results of the washing test made on so-prepared detergents are shown in Table 4.

Table 4

Detergent	*Washing Power Index*
3—(0) (reference detergent)	100
3—(1) (present invention)	103
3—(2) (present invention	103.5
3—(4)	100
3—(5)	100
3—(6)	100

Example 5

A phosphorous-free, weakly alkaline detergent was prepared according to the following recipe.

Sodium linear-dodecylbenzene-sulfonate	15% by weight
Sodium alkylethoxy-sulfate (C_{14}—C_{15}, EO—3 moles)	5% by weight
Builder and enzyme (see Table 5)	20% by weight
Sodium silicate	15% by weight
Sodium carbonate	15% by weight

Carboxymethyl cellulose	1.5% by weight
Polyethylene glycol	1.5% by weight
Fluorescent dye	0.5% by weight
Glauber salt	balance
Water	5% by weight

The results of the washing test are shown in Table 5.

Table 5

Builder	*Enzyme*	*Washing Power Index*
sodium tripolyphosphate, 20%	—	100 (reference detergent)
sodium citrate, 20%	—	98
zeolite type 4A, 20%	—	98.5
sodium citrate, 15%	(6), 5%	98.5
zeolite type 4A, 15%	(6), 5%	98.5
sodium citrate, 15%	(1), 5%	102 (present invention)
sodium citrate, 15%	(2), 5%	102.5 (present invention)
zeolite type 4A, 15%	(1), 5%	101.5 (present invention)
zeolite type 4A, 15%	(2), 5%	102 (present invention)

Example 6

Detergents were prepared according to the recipe adopted in Example 3 by using combinations of enzymes. The results of the washing test made on these detergents are shown in Table 6.

Table 6

Detergent	*Combination of Enzymes (Right Number Indicates % of Enzyme)*	*Washing Power Index*
2—(2) (reference detergent)	(2)=2	100
2—(2)/(4) (present invention	(2)/(4)=1/1	100.5
2—(2)/(5) (present invention	(2)/(5)=1/1	100.5
2—(2)/(6) (present invention)	(2)/(6)=1/1	101
2—(2)/(4)/(6) (present invention)	(2)/(4)/(6)=2/1/1	101.5
2—(2)/(5)/(6) (present invention	(2)/(5)/(6)=2/1/1	101.5
2—(4)/(5)/(6)	(4)/(5)/(6)=2/1/1	98

Example 7

A weakly alkaline powdery detergent for clothing was prepared according to the following recipe.

Sodium alkyl-sulfate ($\overline{C}$=14.5)	15% by weight
Sodium alkylethoxy-sulfate ($\overline{C}$=14.5, $\overline{EO}$=3)	5% by weight
Soap (beef tallow type)	2% by weight
Sodium pyrophosphate	18% by weight
Sodium silicate	13% by weight
Sodium carbonate	5% by weight
Polyethylene glycol	2% by weight
Fluorescent dye	0.2% by weight
Glauber salt	balance
Magnesium silicate	1% by weight
Water	5% by weight
Enzyme	2% by weight
Sodium percarbonate	15% by weight

The results of the washing test made on so-prepared detergents are shown in Table 7.

Table 7

Detergent	*Enzyme*	*Washing Power Index*
6—(6) (reference detergent)	(6)	100
6—(1) (present invention)	(1)	102.5
6—(2) (present invention)	(2)	103

Claims

1. A detergent composition which includes an alkali cellulase.

2. A detergent composition as claimed in Claim 1, in which said alkali cellulase has an optimum effectiveness at a pH of 8.0 to 11.5.

3. A detergent composition as claimed in Claim 1, in which said alkali cellulase is produced by a Bacillus N fungus or a cellulase 212-producing fungus belonging to the genus Aeromonas.

4. A detergent composition as claimed in Claim 1, which contains 0.01 to 70 wt.% of said alkali cellulase having an enzymatic activity of at least 0.001 unit/mg solid.

5. A detergent composition as claimed in Claim 1, which contains said alkali cellulase in an amount of 0.1 to 1000 units per liter of the composition.

6. A detergent composition as claimed in Claim 1, which further comprises one or more of the following surfactants, divalent metal ion sequestering agents, alkali agents, inorganic electrolytes, antiredeposition agents, bleaching agents, enzymes, bluing agents, fluorescent dyes, caking-preventing agents, masking agents for factors which inhibit the alkali cellulase activity, activators for the alkali cellulase, antioxidants, solubilizers and other conventional additives.

7. A detergent composition as claimed in Claim 1, in which said alkali cellulase is extracted from the hepatopancreas of a marine mollusc.

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